

# Vol 4, No 1

#### **Winter 2007**

The San Francisco Bay Mercury News, an electronic newsletter issued annually, is a compilation of mercury research activities currently underway in the Bay Area. The newsletter is distributed by the San Francisco Estuary Institute as part of the Regional Monitoring Program.

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# Introduction

Welcome to the fourth issue of the San Francisco Bay Mercury News! The purpose of this electronic newsletter is to foster communication and collaboration among scientists, regulators, and stakeholders by providing summaries of current mercury monitoring activities in the Bay area. Scientists have provided summary paragraphs regarding the purpose of their work, updates to on-going projects and recently accomplished milestones. Contact information follows each project summary. If you missed the first three issues of the newsletter, you can download them from the SFEI web site at:

http://www.sfei.org/rmp/mercury\_newsletter/HgNews\_home.html

SFEI welcomes contributions to the newsletter. If you have a summary for the newsletter or questions or comments, please e-mail or call Meg Sedlak at SFEI (<u>meg@sfei.org</u> or tel. ((510) 746-7345). Also if you did not receive this newsletter from SFEI directly and you would like to subscribe to this newsletter, please visit the SFEI website to register for the San Francisco Bay Mercury News. Similarly, if you received this newsletter erroneously, you may unsubscribe by going to our web site.

# In This Issue...

# **Upcoming Conferences/Meetings**

1. Fourth Annual SF Bay Mercury Coordination Meeting, Thursday, February 22<sup>nd</sup>, 2007 at the East Bay Community Foundation, De Domenico Building 200 Frank H. Ogawa Plaza, Oakland, CA – Sign up now!

The fourth annual San Francisco Bay Mercury Research Coordination Meeting is rapidly approaching. The meeting will be held this year on February 22nd, 2007 at the East Bay Community Foundation, De Domenico Building 200 Frank H. Ogawa Plaza in Downtown Oakland. The meeting will consist of short presentations by a variety of scientists and regulators from 9 am until approximately 5 pm (lunch will be provided). The draft agenda will be sent out shortly and posted on the SFEI web site. If you would like to present at this event, please contact Meg Sedlak (meg@sfei.org). If you would like to register for this event, please register on-line at:

http://www.sfei.org/rmp/mercurymeeting/2007 4thAnnual/index.html

Please RSVP by February 16th, 2007.



#### 2. San Francisco Bay Regional Water Quality Control Board Updates

#### Statewide Mercury Regulatory Actions

In February the State Water Board plans to hold public scoping meetings for a mercury offset policy and methylmercury water quality objectives. The offset policy is proposed for mercury dischargers to San Francisco Bay, Sacramento-San Joaquin River Delta and tributaries. It would allow dischargers to perform other activities aside from eliminating more mercury from their discharges than they would be required to remove by applicable technology-based effluent limitations. The water quality objectives policy will consider a methylmercury fish tissue objective, a total mercury water quality objective, a methylmercury water quality objective, or some combination of these objectives. Subsequent to State Board adoption of this policy, each of the nine Regional Water Boards would then revise or establish mercury water quality objectives in accordance with this statewide policy. Additional information is posted on the State Water Board website at: <a href="http://www.waterboards.ca.gov/">http://www.waterboards.ca.gov/</a> (under 'water news').

#### San Francisco Bay Region Mercury Regulatory Actions

*Breaking news Walker Creek watershed mercury TMDL was adopted by the Water Board on January 23, 2007.* This watershed contains the Gambonini mine – unpublished data indicates that geotechnical slope stabilization of the waste pile and site revegetation *has reduced mercury loads by 90%.* The Board action established fish tissue water quality objectives protective of piscivorous wildlife which also protect humans who consume watershed fish. The TMDL allocations include methylmercury in the water column of Soulajule Reservoir (0.04 ng MeHg per L), and total mercury in suspended sediments from the Gambonini Mine Site (5 mg/kg HgT) and from Walker Creek and their tributaries (0.5 mg/kg HgT).

Tomales Bay – Following on the heels of the Tomales Bay pathogens TMDL (approved by U.S. EPA), and the Walker Creek watershed mercury TMDL, staff is beginning the initial (data analysis) phase of the Tomales Bay mercury, nutrients and sediment TMDL.

San Francisco Bay – Fish tissue water quality objectives and mercury TMDL adopted by SFBay Water Board in August 2006. It awaits consideration for approval by State Water Board.

Guadalupe River watershed – Staff is preparing the documents for peer review, to include a draft Basin Plan amendment, fish tissue water quality objectives modeled after Walker Creek's, and minor modifications to the January 2006 TMDL Project Report in response to public comments.

San Francisco Bay TMDL website: http://www.waterboards.ca.gov/rwqcb2/tmdlmain.htm

#### Central Valley Region Mercury Regulatory Actions

Sulphur Creek – In March 2007 the Central Valley Water Board will hold a public hearing to consider a determination that certain beneficial uses (notably MUN – drinking water supply) are not applicable in the appropriately named Sulphur Creek, and establish site-specific water quality objectives for mercury in Sulphur Creek, a tributary to Bear Creek in the Cache Creek watershed. The Cache Creek watershed mercury TMDL was previously adopted by the Central Valley Water Board.

Sacramento-San Joaquin Delta Methylmercury TMDL – Board Workshop mid-March 2007. The Central Valley Water Board will hold a public workshop to discuss the development of an amendment to the Water Quality Control Plan (Basin Plan) for the control of methyl and total mercury in the Sacramento-San Joaquin Delta Estuary.

Central Valley TMDL website: http://www.waterboards.ca.gov/centralvalley/programs/tmdl/

#### Contact information:

Carrie Austin, San Francisco Bay Regional Water Quality Control, CAustin@waterboards.ca.gov

# 3. Characteristics of Mercury Load in the Guadalupe River: What Can Four Years of Data Tell Us?

Every year, an average of 530 kg of total mercury is estimated to enter San Francisco Bay from three main external pathways: 1. Urban runoff, 2. the Sacramento-San Joaquin River system, and 3. the Guadalupe River. Data collected by SFEI indicates that the Guadalupe River alone accounts for approximately 30% of this load and we presently estimate that urban runoff accounts for another 20%. With a renewed focus on local tributaries, scientists are being asked to answer more complex questions such as where exactly within the urban landscape or abandoned mine areas are mercury sources located? What is the process of mercury release from these sources? Once released, how does mercury travel from source areas to the Bay? What are the temporal and spatial patterns of transport in our stormwater conveyance systems? What portion of the total mercury load is dissolved, fine and coarse particulate, and methylmercury? What can be done to stop release or to capture mercury before it enters the Bay?

With funding provided by the RMP, CEP, USACE, SCVWD, and SCVURPPP, SFEI has been sampling floods in the Guadalupe River since November 2002 at USGS gauge number 11169025 at Highway 101. Water samples have been analyzed for total mercury (n=164), total dissolved mercury (n=64), total methylmercury and dissolved methylmercury (n=61) and sediment bed load samples have been analyzed for total mercury (n=8) on eight grain size classes from <0.0625mm to >3.8mm. Although primarily designed as a small tributary loading study by the Sources Pathways and Loadings Work Group of the Regional Monitoring Program, data from this study can be used to provide answers to or hypotheses about some of the questions listed above.

Measured total mercury concentrations peaked at 18,673 ng/L over the four study years and 18 samples spread across three years had concentrations between 1,000-16,000 ng/L. Measured total methylmercury concentrations varied from 0.05 - 1.89 ng/L. Measured particulate methylmercury concentrations ranged between 1.1-19.8 ng/g. Measured total mercury concentrations in the bed load sediments ranged between 0.03 and 1.8 µg/g (median of eight samples) and increased with decreasing grainsize. Watercolumn total mercury load varied between years in relation to climatic forcing: water year 2003 (116 ± 36 kg), water year 2004 ( $15 \pm 4.5$  kg), water year 2005 ( $8 \pm 2.5$  kg), and water year 2006 ( $26 \pm 8.0$  kg). The largest flood occurred on December 16, 2002 and accounted for 6% of the 4-year load and the two largest floods accounted for 18% of the load. The five floods that occurred in the second half of December, 2002 accounted for 32% of the total 4-year load. Total methylmercury load was 0.5% of the water year 2005 load and 0.3% of the in water year 2006 load. On average, total dissolved mercury load accounted for 3% of the annual load. Thus, the potentially bioavailable mercury (dissolved and methylated forms) is approximately 3.5% of the total annual load. The bioavailability of fine particulate inorganic mercury is still debated. Bed load mercury accounted for 1% of the total load in water year 2005 (the only year it was measured). Our results imply that management of loads could be focused on just a few floods when most of the transport occurs.

# Contact Information:

Lester J. McKee, Ph.D. San Francisco Estuary Institute, lester@sfei.org.

# 4. Mercury Cycling Studies Associated with the Hamilton Wetland Project

Restoration of wetland habitat around San Francisco Bay must be evaluated in the context of the potential impact of export of Hg-species to the Bay-Delta ecosystem. We are currently providing San Francisco Bay Long Term Management team with information on linkages between Hg biogeochemistry and wetland restoration in San Pablo Bay in the context of the San Francisco Bay fishery and endemic threatened and endangered species. This information provides environmental managers and policy makers the best science available for planning and decision support.

While over 90% of the total mercury (THg) in sediment and soil samples is inorganic, over 95% of THg in top predators is methyl mercury (MeHg). MeHg biomagnifies up food webs and is a neurotoxin. Standing MeHg pools are the product of primarily anaerobic (sulfate-reducing) bacteria that methylate Hg<sup>2+</sup> and many bacteria that demethylate MeHg. Factors that affect these competing reactions regulate, in part, the incorporation of MeHg into food webs. Little quantitative data are available on the factors that control net MeHg production wetlands and on the processes and rates at which MeHg bioaccumulates at different trophic levels.

Pre-construction data were collected at the Hamilton Wetland Restoration Project (HWRP) in a nearby, established, reference wetland, China Camp. The following work was completed:

- The temporal and spatial variability in the concentrations of Hg species were measured in bare and vegetated sediments. On-site methylation and demethylation rates were determined.
- A new Diffusive Gradient Thinfilm (DGT) device was developed to rapidly measure Hg species in water and sediment pore-water. DGT is a device that enables the collection of high-resolution information on sediment biogeochemistry needed to better understand physico-chemical processes that influence net MeHg production. DGT data enable the calculation of the net diffusive flux of Hg species from sediment into the water column.
- An advanced understanding of the fate and effects of Hg species into salt marsh food webs was attained by determining the Hg species fluxes through the live and standing dead mass, and litter of two predominant marsh plants.
- Biomagnification of Hg species was quantified, and the existence of two food webs was postulated, i.e.,
  (1) A Spartina-deteritus-based semi-aquatic and near-shore aquatic, and (2) A Salicornia-associated lower-high tidal marsh.

Ultimately, mass balances will be calculated, food web structure quantified, and management options formulated, with data integration using a screening-level model approach. The mass balance will provide the understanding of fate of Hg species in wetlands.

**Contact Information** 

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### 5. What Controls Methylmercury Production in Brackish Tidal Wetlands of the Petaluma River -The Importance of Vegetation, Subhabitats, and Marsh Age

Our data from linked studies of different subhabitats in San Francisco Bay consistently demonstrate that methylmercury (MeHg) concentrations and rates of productions are highest in salt marsh sediments and lowest in the central delta. Rates of mercury methylation in salt marshes were 1-2 orders of magnitude greater in densely vegetated interior marsh sites than in marsh edge sites along sloughs. MeHg concentrations and Hg(II)-methylating bacterial activity associated with pickleweed-dominated (Salicornia virginica)salt marsh plains were strongly correlated with plant root density and growth rates. Paired

vegetated/devegetated plot experiments conducted in these salt marsh settings demonstrated that the removal of photosynthetic-inputs mediated sediment biogeochemistry and significantly reduced rates of MeHg production, up to 30 fold.

Collaborators:

Lisamarie Windham-Myers, Ph.D. and Mark C Marvin-DiPasquale, Ph.D, U.S. Geological Survey

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# 6. Benthic Mercury Biogeochemistry: A Bay-wide Perspective

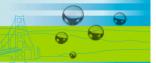
Mercury researchers at the U.S. Geological Survey in Menlo Park have been guite busy over the past few years, as they are involved in multiple parallel mercury studies throughout the San Francisco Bay and its watershed. The common question being asked throughout these studies is "What ultimately controls methylmercury production in a particular aquatic habitat and at a particular time". It turns out that the answer to this seemingly simple query is that "it depends" on the a large suite of environmental factors that ultimately control a) the presence and activity of benthic bacteria that methylate inorganic 'reactive' mercury (Hg(II)<sub>R</sub>), and b) the availability of Hg(II)<sub>R</sub> to those bacteria. So it is no surprise that when we look across a large, complex aquatic ecosystem like the San Francisco Bay, where each one of these potentially influential factors varies in time and space, the corresponding result is a wide range of Hg(II)methylation rates, with some factors being more important than others at various points along the timespace continuum, and no one factor ultimately controlling the methylation process in all cases. By using consistent methods across all studies to assess Hg(II)-methylation rates, microbial processes (e.g. sulfate and iron reduction), and sediment geochemistry (of carbon, sulfur, iron and mercury), the USGS research group is developing a more predictive understanding of the methylation process throughout the ecosystem. Synthesizing data from across these multiple studies, the following conclusions have been reached. 1) The Hq(II)<sub>R</sub> pool size is depressed under reducing sediment conditions and elevated under oxidized conditions. 2) The central delta has generally low MeHg production, due to a comparatively low Hg(II)<sub>R</sub> pool size. 3) Freshwater rivers, upstream of the central delta, exhibit comparatively higher MeHg production due to a higher Hg(II)<sub>R</sub> pool size. 4) Saltmarsh settings, downstream of the central Delta, are zones of enhanced MeHg production, due to very active populations of Hg(II)-methylating bacteria. 5) The presence/absence and type of vegetation in a given wetland setting exerts a strong control on MeHg production, as both microbial activities and Hg(II)R pool size are impacted by strong biogeochemical gradients that exist in the plant root zone. 6) Areas that experience periodic inundation (seasonal floodplains and tidal marshes) exhibit enhanced MeHg production compared to nearby areas that are continuously submerged.

# Contact Information:

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# 7. Update on the San Jose/Santa Clara Water Pollution Control Plant Mercury Fate and Transport Study

Since October 2004, over 700 aqueous samples have been collected and analyzed for total, total methyl, and dissolved mercury and parallel samples for TSS, sulfide, chloride and sulfate. A subset of samples have also been analyzed for dissolved methylmercury. Thirty-two sludge samples have been collected for analysis of total mercury, methylmercury, and total solids. Blank samples were collected to document avoidance of cross-contamination and to ensure the cleanliness of sample bottles, filters, and the sampling apparatus. Quality control and assurance results have shown that cleaning, sampling, and



analytical techniques have effectively delivered uncontaminated, unbiased samples and accurate analytical results.

Phase I studies, which included weekly sampling of 8 process locations, began in October 2004 and concluded in August 2005. Phase II sampling has continued weekly, including monthly sampling of the original 8 stations, and weekly sampling of raw sewage and final effluent. Results show a highly efficient removal rate for total mercury (over 98%) correlated with the removal of suspended solids. Filtered mercury, total methylmercury, and filtered methylmercury concentrations decrease through the process at rates of 53, 97, and 73%, respectively. Flows and concentrations of mercury in digested sludge appear to account for the mercury removal within the limits of uncertainty introduced by difficulties in accurate flow measurement, highly variable raw sewage and sludge concentrations, within-day temporal bias, and process feedback loops. Seasonal trends in mercury and methylmercury output are not evident, probably owing to the relatively constant conditions under which the Plant is operated.

An interim report has been prepared and submitted for independent peer review. Based on that review and recommendations, San Jose staff will prepare a list of potential additional activities to better estimate the mass balance of mercury through the Plant. The 2006 progress report and interim report will be available by the end of February at http://www.sanjoseca.gov/esd/pub\_res.htm.

### Contact Information:

James Downing, City of San Jose Environmental Services Watershed Protection Division, 170 W. San Carlos St., San Jose, CA 95113. Phone: (408) 277-2765, james.downing@sanjoseca.gov

# 8. SRCSD Mercury Bioaccumulation Study

The Sacramento Regional County Sanitation District (SRCSD) is conducting a novel study to detect and quantify any localized bioaccumulation of mercury associated with its wastewater discharges into the lower Sacramento River. Field work conducted monthly between July and November of 2006 by Applied Marine Sciences focused on sampling several thousand resident and transplanted (suspended) clams at five stations upstream and downstream of the wastewater discharge. Sediment and water column samples were also collected at these sites. Biosentinel fish were collected locally and regionally in collaboration with Calfed research by UC Davis' Darell Slotton to provide a regional context to local conditions. UC Davis' Fraser Shilling is surveying local anglers and fish consumers. Clam tissue samples are currently being analyzed for mercury content by Studio Geochimica in Seattle. Results are expected by June 2007.

# Contact information:

Vicki Fry, SRCSD, 916-876-6113, fryv@SacCounty.net; or Juliet Simpson, Larry Walker Associates, 530-753-6400, juliets@lwa.com.

# 9. Sacramento Regional Wastewater Treatment Plant Methyl Mercury Study

The mercury and methylmercury (MeHg) Total Maximum Daily Load (TMDL) for the Sacramento San Joaquin River Delta proposes to establish a methylmercury control program. Since there aren't any well-defined ways to do this, implementation actions necessarily start with management questions and studies to answer the management questions. The Sacramento Regional Wastewater Treatment Plant (SRWTP) recently conducted a study to evaluate the fate and transport of MeHg at the facility: One key aspect of the study was to determine if the MeHg load from the solids treatment train had any significant impacts to the fate and transport. Filtered and unfiltered methylmercury and total mercury samples were analyzed throughout the SRWTP, and the data were used to calculate loads and the solid-liquid partition coefficient (Kp) of methylmercury at different points within the treatment train. While some methylation was occurring in the sludge digesters, very little was escaping via the supernatant return, accounting for only about 13% of the methylmercury load to the head works. The key factor that caused an increase in the

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methylmercury to total mercury ratio from influent to effluent was the Kp. Methylmercury within the treatment plant was found to have a Kp about tenfold less than that of total mercury. Since inorganic mercury sticks to particles much more readily than methylmercury, a treatment plant which removes particles will preferentially remove inorganic mercury, increasing the methylmercury / total mercury ratio in the process. A mass balance helped characterize the fate of methylmercury within the treatment plant. There was no net production of MeHg and in fact significant removal of Hg and MeHg at the SRWTP was measured consistently. The implications for treatability of methylmercury in discharge are not known at this time.

These findings were presented at WEFTEC 2005; copies of the paper are available. Details can be obtained from Khalil Abusaba (contact information below) or Mitch Maidrand of the SRWTP at (916) 875-9083, e-mail maidrandm@saccounty.net.

<u>Contact Information</u>: Dr. Khalil Abusaba, Brown and Caldwell Associates, E-mail: KAbusaba@BrwnCald.com

### 10. Mercury Effects on Avian Reproduction in San Francisco Bay

The risks of methyl mercury bioaccumulation and its toxic effects on reproduction are likely greater in waterbirds than other wildlife in San Francisco Bay. We examined mercury concentrations in five waterbirds common to San Francisco Bay: surf scoters, American avocets, black-necked stilts, Forster's terns, and Caspian terns. Using telemetry, diet, and stable isotope analyses, we quantified key habitats, locations, and prey items utilized by pre-breeding and breeding waterbirds. We captured and collected birds at several sites throughout the estuary, including North, Central, and South Bay regions. We examined mercury concentrations in adults, chicks, and eggs, as well as those in their fish and invertebrate prey. We also monitored nest success of the four locally breeding species (avocets, stilts, and Forster's and Caspian terns) at several colonies throughout the Estuary. We found that mercury concentrations were highest in Forster's Terns, followed by stilts, Caspian terns, scoters, and avocets. Sites within the extreme South Bay were substantially elevated, followed by North Bay and Central Bay sites. We also found that mercury concentrations in terns were strongly correlated with oxidative stress biomarkers in liver, kidney, and brain, indicating cellular level stress. Using a risk factor analysis, we estimated that risk to reproductive impairment was especially high in the South Bay where 27%, 22%, 10%, and 1% of Forster's tern, stilt, Caspian tern, and avocet populations were at or above high risk, respectively. Moreover, 58% of breeding Forster's terns were considered to be at or above high risk in the South Bay, indicating that more thorough quantification of effects of methyl mercury on reproductive success are necessary.

#### Collaborators:

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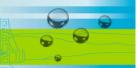
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Contact information:

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# 11. Mercury in Biosentinel Fish in San Francisco Bay

The Hg TMDL is a major effort to reduce mercury accumulation in Estuary fish, and there is concern that extensive tidal marsh restoration could increase mercury in the food web. To evaluate spatial and temporal variation in risk posed to wildlife by bioavailable Hg, we are monitoring small fish in nearshore Bay locations. Annual monitoring has been funded from 2005 to 2008. Monitoring focuses on small fish species representing a range of vagility and salinity tolerance at nearshore and channel locations in San Francisco Bay. Of 97 composite samples captured in 2005, 39 (i.e., 40%) had total Hg concentrations higher than a proposed 0.03 ppm (wet weight) TMDL target threshold. Mississippi silverside (*Menidia audens*) had higher Hg concentration than other species tested, and Bay gobies (*Lepidogobius lepidus*) had lower concentrations. For Mississippi silverside and cheekspot gobies (*Ilypnus gilberti*), concentrations were significantly higher at Alviso Slough than stations further north, and these difference could not be attributed to differences in fish size. To further characterize the spatial variation observed in 2005, 2006 monitoring included 22 locations from Lower South Bay to San Pablo Bay. Results indicate that future TMDL-related monitoring designs and interpretation should explicitly account for variations among fish species, size, and sampling location.

### Collaborators:

Ben K. Greenfield<sup>1</sup>, Andy Jahn<sup>2</sup>, J. Letitia Grenier<sup>1</sup>, Seth Shonkoff<sup>1</sup>, Mark Sandheinrich<sup>3</sup>

1. SFEI; 2. 1000 Riverside Drive, Ukiah, CA; 3. River Studies Center, University of Wisconsin – La Crosse Contact information:

# Contact information:

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# 12. The Role of Phytoplankton in Mercury Cycling and Bioavailability in San Francisco Bay

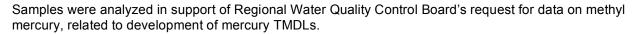
Previous studies on mesocosms and lakes that show that the abundance of phytoplankton may be a key factor controlling concentrations of methyl mercury (MeHg) in fish (Chen et al. 2005; Pickhardt et al. 2002). To evaluate the effects of a change in phytoplankton biomass, we sampled during the spring 2003 phytoplankton bloom in South San Francisco Bay. Unusually warm, calm conditions lead to one of the largest phytoplankton blooms on record. Concentrations of dissolved (<0.45µm) MeHg were depleted by the bloom, which peaked on 04 March with chlorophyll a concentrations >150µL-1. This study indicates that the recently observed increase in phytoplankton biomass in the estuary (Cloern et al. 2006) could affect mercury bioavailability by transferring MeHg from water to phytoplankton, increasing MeHg concentrations in water and particles as algae decay, and entraining HgT in the estuary through particulate scavenging.

# Contact information:

Alison Luengen, UCSC. E-mail: Luengen@etox.ucsc.edu

# 13. Analysis of POTW Effluents for Methyl Mercury

Water Quality analysis of POTW (publicly owned treatment works) effluent with respect to methyl mercury is fairly new. Even though POTWs are not a large source of mercury in the aquatic environment, EPA 303C regulations require adoption of water quality criteria that are protective of beneficial uses of water bodies. As protection of beneficial uses with respect to mercury involves Total Maximum Daily Load allocations (TMDLs), it becomes necessary to evaluate all sources. A review of the method performance of EPA's draft methyl mercury method (1630) was conducted as it applied to the analyses of wastewater treatment plant effluents in the San Francisco Bay and Sacramento and San Joaquin River's Delta areas.



Most data on methyl mercury in the environment is from trace metals specialty/ research labs, or government and academic labs for research purposes. Routine analysis of wastewater for methyl mercury is new. Because we now have a substantial POTW effluent data set, we include a brief report of the performance of the draft method 1630 in the wastewaters we have analyzed.

Summary data includes the last two hundred matrix spikes averaging 93% in matrix; relative percent difference of the last 100 MS/MSD spikes average 9% in matrix. Laboratory Control Standards (spiked reagent water) average 105% recovery.

<u>Contact Information</u>: Peter Halpin, Caltest Analytical Laboratory 1885 North Kelly Rd. Napa, CA 94558. (707) 258-4000. E-mail: <u>Pete\_Halpin@caltestlabs.com</u> Collaborators on this project include: Christine Horn and Tiffiny Crenshaw.

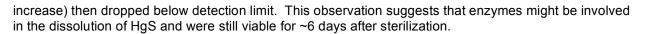
### 14. Mercury and Methylmercury Processes in North San Francisco Bay Tidal Wetland Ecosystems

This project to study mercury and methymercury processes in wetlands of the Petaluma River and San Pablo Bay was funded in 2004, with field work in 2005 and 2006. All field work is now complete, with laboratory analysis ongoing, and draft and final reporting in late 2007/early 2008. Partners in this project include SFEI, USGS Menlo Park, USGS Biological Resources Division, USGS Wisconsin, and Avocet Associates. A primary interest of this project is to examine processes that lead to mercury exposure and accumulation in wetland biota. This project has examined Hg and MeHg concentrations in the sediments, water and biota of tidal marshes along a salinity gradient up Petaluma River. Influences of seasonal and interannual variation in environmental parameters on Hg geochemistry and bioaccumulation will also be examined. Physiographic features and resulting hydrologic and vegetative differences within and among habitat elements in wetlands are also expected to impact Hg/MeHg geochemistry, subsequent transport, and uptake by biota. This knowledge may be useful for anticipating possible impacts of restoration projects, and for identifying factors that can allow us to minimize or mitigate negative impacts to the ecosystem.

Contact information: Donald Yee at SFEI (donald@sfei.org).

# 15. Bacterially Mediated Breakdown of Cinnabar and Metacinnabar and Environmental Implications

Mercury in the forms of cinnabar ( $\alpha$ -HgS) and metacinnabar ( $\beta$ -HgS) is generally considered to be unreactive and of little environmental concern. To determine if this current belief is valid, a consortium of bacteria (including a *Thiomonas intermedia*-like bacterium) was taken from the acid mine drainage (AMD) pond at the New Idria Hg Mine, San Benito Co., CA, and inoculated into filter-sterilized AMD pond water containing either ground cinnabar or metacinnabar crystals (< 45 µm in diameter), with sampling occurring every 3 days. Under aerobic conditions the samples showed a pronounced increase in aqueous Hg concentration over background water concentrations (390(±20)ng/L). Bacteria growing on  $\alpha$ -HgS increased the Hg concentration to 297(±10) g/L, while bacteria growing on  $\beta$ -HgS resulted in levels of 4.6(±0.2) mg/L; both maxima occurred at 18 days incubation. Experiments conducted with (1)  $\alpha$ -HgS or  $\beta$ -HgS in the presence of killed bacteria (anaerobic), (2)  $\alpha$ -HgS with pond water (abiotic), and (3)  $\beta$ -HgS with pond water (abiotic) showed drops in aqueous Hg to below the detection limit (0.1ng/L) within 12 days. Anaerobic growth of the bacterial consortium showed a pattern similar to those of the water and HgS experiments, except that Hg levels dropped below detection limit within 6 days. These combined results suggest that HgS degradation by this bacterial consortium is an aerobic process. Killed bacteria incubated aerobically showed a slight increase in Hg levels over background water levels (< 10x



The New Idria AMD pond consists of an inlet stream and an outlet pipe, separated from each other by ~3m. The Hg concentration in the ferrihydrite-rich sediments at the inlet is 37 mg/kg, dry weight, while the concentration at the outlet is 216 mg/kg, dry weight. Surface water concentrations of Hg at the AMD pond are generally <100 g/L, suggesting that the sediments sequester Hg. During the wet season (October-March), the AMD pond receives considerable amounts of run-off from precipitation, which flushes Hg associated with ferrihydrite out of the region into the San Joaquin river system, representing a possible mode of Hg transport out of the New Idria Hg mining district.

### Collaborators:

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### **16. Complexation of Mercury in Freshwater Systems**

UC-Santa Cruz ecological toxicity group is continuing studies investigating the complexation of Hg(II) in freshwater systems, and evaluating ligand sources and identity. A second project that is underway is using a bioreporter to study how complexation affects uptake of mercury into cells.

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#### 17. The CBDA Fish Mercury Project: A Pilot Program for Monitoring, Stakeholder Involvement, and Risk Communication Relating to Mercury in Fish in the Bay-Delta Watershed

This is a three year CalFed funded, collaborative project for monitoring mercury concentrations in sport fish and biosentinel fish, developing fish consumption advisories, and communicating associated health risks to affected communites. To date, we have completed two years of sport fish and biosentinel fish sampling (2005 and 2006) and are in the planning stages for our last sampling effort (2007). The FMP uses an integrated monitoring approach where stakeholders provide input in the development of the sampling plan, including sampling locations and popular sport fish species. Stakeholders include members of community based organizations (CBOs), ecosystem managers, and scientists. The first year reports on the sport fish and biosentinel sampling efforts, and other associated documents, are available on the project web site (http://www.sfei.org/cmr/fishmercury/).

The Office of Environmental Health Hazard Assessment (OEHHA) has recently released a fish consumption advisory for the lower Feather River and has released a draft advisory for the San Joaquin River and South Delta. The Department of Health Services Environmental Health Investigations Branch (EHIB) is continuing with outreach and education efforts and has recently provided funding to CBOs for developing community specific educational materials. We are holding our 2007 Annual Meeting on June 5 through 7 in the Sacramento area. This is a three-day meeting that will focus on peer review of the 2007 sampling plan and project deliverables. There

will be an increased effort to integrate other local mercury projects into this meeting in order to look at the mercury problem on an ecosystem scale. This project will continue through 2008.

# 18. Songbirds as Biosentinels for Tidal Wetlands: Initial results from North and South San Francisco Bay

Uncertainty regarding the effect of wetlands on bioaccumulation of mercury in food webs creates a need for biosentinel species that are effective for monitoring trends in mercury exposure in and near wetland restoration areas. We are developing a suite of habitat-specific biosentinels to monitor change in the South Bay Salt Pond Restoration Project area and elsewhere in the San Francisco Estuary. Among species being considered as biosentinels are the obligate tidal marsh Song Sparrows endemic to the Estuary. These songbirds are top resident predators in the inter-tidal wetlands fringing the Bay. They reside and feed in the vegetated marsh plain habitat. Results from sampling sparrows and other songbirds at 5 marshes in North and South San Francisco Bay during 2006 indicate clear patterns of mercury bioaccumulation among species and marshes. Overall, the median concentration in sparrow blood (0.31 ug/g wet weight, n = 37) exceeded the average mercury in small fish (whole body) from an RMP 2005 study by a factor of 6, even though they occupy similar trophic levels. The median warbler value (0.42 ug/g ww, n = 4) was on a par with that of striped bass (RMP 2003 data), and the single wren sample (0.82 ug/g ww) was similar to the median for leopard shark (RMP 2003 data).

- <sup>o</sup> Warblers had higher total mercury in blood than sparrows, and one wren sample was nearly double the median warbler concentration. We hypothesize inter-specific differences are related either to trophic level or differences between a more epibenthic marsh plain invertebrate food web for sparrows and a more terrestrial arthropod food web for wrens and warblers.
- ° Variation in sparrow mercury among marshes was significant, with higher concentrations from the Petaluma River marshes and lower concentrations from marshes in the Alviso area. This pattern is the opposite of the pattern in small fish between North and South Bay.
- <sup>o</sup> Variance among sparrow mercury concentrations within a marsh was higher in the northern Petaluma sites. We hypothesize that inter- and intra-marsh variation may be related to marsh plain elevation. Elevation may correlate with several ecological factors, including frequency and duration of inundation, amount of organic matter in sediment (especially peat), frequency of wetting from ground water fluctuations, types of prey available, etc.

Data are not yet sufficient to evaluate these hypotheses, but these initial results indicate that resident marsh songbirds may yield helpful information for monitoring and to guide further process studies

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